



HAL
open science

High Pressure Inside Nanometer-Sized Particles Influences the Rate and Products of Chemical Reactions

Matthieu Riva, Jianfeng Sun, V. Faye Mcneill, Charline Ragon, Sebastien Perrier, Yinon Rudich, Sergey Nizkorodov, Jianmin Chen, Frédéric Caupin, Thorsten Hoffmann, et al.

► **To cite this version:**

Matthieu Riva, Jianfeng Sun, V. Faye Mcneill, Charline Ragon, Sebastien Perrier, et al.. High Pressure Inside Nanometer-Sized Particles Influences the Rate and Products of Chemical Reactions. *Environmental Science and Technology*, 2021, 55 (12), pp.7786-7793. 10.1021/acs.est.0c07386 . hal-03363154

HAL Id: hal-03363154

<https://hal.science/hal-03363154v1>

Submitted on 3 Oct 2021

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

1 **High pressure inside nanometre-sized particles influences the rate**
2 **and products of chemical reactions**

3 Matthieu Riva^{†,*}, Jianfeng Sun^{†,§}, V. Faye McNeill^{||}, Charline Ragon[†], Sebastien Perrier[†], Yinon
4 Rudich[⊥], Sergey A. Nizkorodov[#], Jianmin Chen[§], Frederic Caupin[∇], Thorsten Hoffmann^{°,*}, Christian
5 George^{†,*}

6 [†] Univ. Lyon, Université Claude Bernard Lyon 1, CNRS, IRCELYON, F-69626, Villeurbanne, France.

7 [§] Shanghai Key Laboratory of Atmospheric Particle Pollution and Prevention (LAP3), Department of
8 Environmental Science & Engineering, Fudan University, Shanghai 200433, China.

9 ^{||} Department of Chemical Engineering and Department of Earth and Environmental Sciences,
10 Columbia University, New York, NY 10025 USA

11 [⊥] Department of Earth and Planetary Sciences, Weizmann Institute, Rehovot 76100, Israel.

12 [#] Department of Chemistry, University of California, Irvine, CA 92694, USA.

13 [∇] Université de Lyon, Université Claude Bernard Lyon 1, CNRS, Institut Lumière Matière, F-69622,
14 Villeurbanne, France.

15 [°] Department of Chemistry, Johannes Gutenberg-Universität, Mainz, Germany.

16 **Keywords:** SOA, mass spectrometry, heterogeneous chemistry, pressure, new particle
17 formation

18 **Abstract**

19 The composition of organic aerosol has a pivotal influence on aerosol properties such as toxicity, and
20 cloud droplets formation capability, which could affect both climate and air quality. However, a
21 comprehensive and fundamental understanding of the chemical and physical processes that occur in
22 nanometre-sized atmospheric particles remains a challenge that severely limits the quantification and
23 predictive capabilities of aerosol formation pathways. Here, we investigated the effects of a
24 fundamental and hitherto unconsidered physical property of nanoparticles – the Laplace pressure. By
25 studying the reaction of glyoxal with ammonium sulphate, both ubiquitous and important atmospheric
26 constituents, we show that high pressure can significantly affect the chemical processes that occur in
27 atmospheric ultrafine particles (i.e., particles < 100 nm). Using high-resolution mass spectrometry and
28 UV/Vis spectroscopy, we demonstrated that the formation of reaction products is strongly (i.e., up to a
29 factor of 2) slowed down under high pressures typical of atmospheric nanoparticles. A size-dependent
30 relative rate constant is determined and numerical simulations illustrate the reduction in the production
31 of the main glyoxal reaction products. These results established that the high pressure inside
32 nanometre-sized aerosols must be considered as a key property that significantly impacts chemical
33 processes that govern atmospheric aerosol growth and evolution.

34

35 **Short Synopsis**

36 High pressure reached inside atmospheric nanometre-sized particles affects their chemistry and
37 therefore their formation and growth.

38 **Introduction**

39 Aerosol particles are a ubiquitous component of the atmosphere, comprising small liquid and solid
40 particles suspended in the air, with diameters that vary from a few nanometres (nm) to several tens of
41 micrometres (μm).¹ Fine atmospheric aerosols ($\text{PM}_{2.5}$, particles with aerodynamic diameter $\leq 2.5 \mu\text{m}$)
42 produce a significant cooling effect in the atmosphere¹⁻³ through two mechanisms: by directly
43 reflecting solar radiation back into space, and by acting as nuclei for the formation of cloud droplets,
44 thereby regulating cloud reflectivity and lifetime.^{2,3} $\text{PM}_{2.5}$ also has a negative impact on air quality and
45 human health, representing the fifth ranking human health risk factor globally.⁴ Fine atmospheric
46 aerosols can either be emitted directly into the air as primary aerosol, or formed in the atmosphere by
47 gas-to-particle conversion and classified as secondary aerosol.^{1,5} The chemical composition of primary
48 and secondary aerosols is mainly dominated by organic and inorganic species (and water at high
49 relative humidity). While the inorganic species are limited to a few compounds (e.g., sulphates and
50 nitrates are the largest contributors to submicron aerosol mass globally), there are thousands of organic
51 compounds in aerosols.⁶ The organic vapours able to grow aerosols by condensation, thus forming
52 “secondary organic aerosol” (SOA), are primarily formed through gas-phase oxidation of volatile
53 organic compounds (VOC) emitted from biogenic and anthropogenic sources.^{1,5} However, the precise
54 components and physicochemical processes involved remain poorly understood. Improving our
55 fundamental knowledge of the chemical and physical processes that govern atmospheric aerosol
56 growth and evolution is crucial to better quantify aerosol growth and properties and hence the effect of
57 aerosols on climate change and impact on air quality.

58 While research is mainly focused on elucidating the processes that control the formation and
59 evolution of SOA, one of the most fundamental properties – the pressure inside atmospheric particles
60 – is currently neglected in aerosol formation and growth models. The Laplace pressure is of central
61 importance for the thermodynamic description of liquids with strongly curved interfaces (i.e.,
62 nanoparticles and nanoscale droplets). It represents the pressure difference of a droplet between the
63 inside and outside. This effect is produced due to surface tension at the interface between a liquid and
64 the gas interface of a curved surface.⁷ The Laplace pressure is proportional to the surface tension and

65 the inverse of the droplet size.⁷ The pressure is a fundamental physical quantity that affects the values
66 of various thermodynamic and kinetic constants of numerous chemical reactions.⁸ The crucial
67 parameters to describe the influence of pressure on chemical reactions can be further broken down,
68 namely the reaction volume (ΔV) and the volume of activation ($\Delta^\ddagger V$). The volume of activation $\Delta^\ddagger V$ is
69 the volume change of the reaction system from the reactants to transition state, and the reaction
70 volume ΔV is the corresponding volume change from the reactants to the products. The former has
71 been studied in particular by Evans and Polanyi in their development of the transition state theory.⁹ As
72 a result, the Laplace pressure is expected to have strong effects on the equilibrium state of any
73 chemical system and may either accelerate or slow a given reaction. In general, processes that lead to a
74 net increase in the molar volume from reactants to products (i.e., $\Delta V > 0$) are thermodynamically
75 suppressed at high pressure, and processes with a positive volume of activation from reactants to
76 transition state are kinetically suppressed at high pressures.¹⁰

77 To investigate the influence of the internal pressure on atmospherically relevant systems, we
78 have considered a well-studied reaction of glyoxal and ammonium sulphate. Glyoxal is among the
79 most abundant oxygenated VOC produced in the atmosphere from the oxidation of biogenic and
80 anthropogenic organic precursors.¹¹ While it was previously considered as too volatile to contribute to
81 SOA formation, recent studies have shown that glyoxal and other small dicarbonyl species can
82 significantly contribute to SOA growth through multiphase chemistry.¹²⁻¹⁸ Since these species are
83 largely produced in the gas phase, condensed phase sinks help explaining an important part of the
84 missing SOA mass predicted by simulations.^{17,23} In the presence of ammonium sulphate these
85 multiphase processes produce light-absorbing complex organic compounds, that contain an imidazole
86 function.^{12,19,20,24} The vast majority of the kinetic studies characterizing atmospheric chemical
87 reactions are conducted in bulk solution,²² and/or in large aerosols,¹⁸ hence earlier studies on glyoxal
88 chemistry were performed at atmospheric pressure. To demonstrate the potential importance of the
89 internal pressure for atmospheric chemical reactions, this study has focused on the chemical
90 characterization of glyoxal chemistry at pressures that simulate the interior of atmospheric
91 nanoparticles (i.e., < 100 nm).

92 **Experimental Methods**

93 The experiments were performed using individual low-density polyethylene bags (VWR). 10 mL bulk
94 samples were introduced into the bags, that were sealed without any air. The solutions mixtures
95 contained 2 M ammonium sulphate ((NH₄)₂SO₄; (99.0%, Sigma Aldrich) and 0.25-2 M of glyoxal
96 (40% in water, Sigma Aldrich), corresponding to a pH of 4. Experimental conditions were selected
97 based on earlier studies which investigated the reaction of glyoxal with ammonium. Although these
98 conditions do not mimic ambient concentrations, we selected this model system and reproduced the
99 currently accepted conditions used in other studies and modified only the pressure at which the
100 reaction took place. For each experiment, two sets of samples were prepared: i) “control” samples
101 were protected from ambient light and kept at room temperature and at atmospheric pressure; ii)
102 “pressure” samples were introduced into a high-pressure closed vessel (or reactor) and pressurized
103 using water at 12.5, 25 or 50 MPa at room temperature (Figure S1). The 5 bags containing 4
104 concentrations and 1 control were pressurized in a high-pressure vessel (OC-1; High Pressure
105 Equipment Company, Erie, Pennsylvania) by a piston screw pump (Top Industry, France). Once the
106 piston reached the desired pressure, the high-pressure vessel was isolated (using valves) in order to
107 obtain a stable pressure during the experiment. The pressure inside the vessel was continuously
108 monitored and remained stable (i.e., less than 5% decrease over each experiment).
109 One set of samples comprises four solutions containing glyoxal (0.25, 0.5, 1 and 2M) and (NH₄)₂SO₄
110 (2M), 1 solution containing only glyoxal (2 M) and one water blank. The blanks were used to identify
111 possible contamination from the bag itself. The results showed that the bags were not degraded by the
112 chemicals (organics, acids, etc.) used in the experiments. The samples were maintained for 3, 6, 12, 18
113 and 24-h. At least three replicates for each condition (concentration, exposure time and pressure) were
114 performed.

115 **UV/Vis characterization.** Kinetic analyses were based on measurements of the absorbance of the
116 reaction mixtures as a function of time over 200-900 nm with a UV/Vis spectrometer (Cary 60,
117 Agilent Technology). Directly after the end of the experiments, the samples were diluted (by a factor
118 of 10) in deionized water to stop/significantly slow down the glyoxal reaction and ensure an optimal

119 quantification (i.e., peak absorbance < 1). The diluted reaction mixtures were taken and placed into 1
120 cm quartz cuvettes. Control experiments were performed (i.e., without dilution) to ensure that the
121 dilution did not modify the composition of the reaction mixtures. The ratio of the peak absorbance of
122 the solution at high pressure and at atmospheric pressure were similar with (e.g., ratio = 0.52, 2Mat 50
123 MPa) and without dilution (ratio = 0.56; 2M at 50 MPa). The absorption band between 260 nm and
124 300 nm was used to probe the formation of light-absorbing compounds produced from the reaction of
125 glyoxal with ammonium ions. Note that using the analytical techniques employed in this study, it was
126 not possible to directly monitor the reactants' concentrations. Therefore, no quantitative data on the
127 thermodynamics were obtained.

128 **Chemical characterization.** Solutions exposed at atmospheric pressure and at high pressures were
129 directly diluted ($\times 10,000$) at the end of the experiments to stop the reaction. Diluted samples were
130 analysed by ultra-high performance liquid chromatography (Dionex 3000, Thermo Scientific) using a
131 Waters Acquity HSS C18 column (1.8 μ L, 100 x 2.1mm) coupled with a Q-Exactive Hybrid
132 Quadrupole-Orbitrap mass spectrometer (Thermo Scientific) equipped with an electrospray ionization
133 (ESI) source operated in negative and positive modes. The mobile phase consisted of (A) 0.1% formic
134 acid in water (Optima[®] LC/MS, Fischer Scientific) and (B) 0.1% formic acid in acetonitrile (Optima[®]
135 LC/MS, Fischer Scientific). Gradient elution was carried out by the A/B mixture at a total flow rate of
136 300 μ L/min: 1% of B for 2 min, a linear gradient was used until 100% of B for 11 min, then 100% of
137 B for 2 min and back to 1% of B in 0.1 min, and to end 1% of B for 6.9 min. Caffeine was used as an
138 internal standard to retrieve the ionization efficiency of the different samples in order to account for
139 the variability of the UPLC/ESI-Orbitrap. The recovery of caffeine was $86 \pm 5\%$ (1 std. dev.) and each
140 sample was corrected for the instrumental variability.

141 **GAMMA simulations.** Calculations were performed using the photochemical box model GAMMA
142 5.0^{25,26} to simulate the formation of light-absorbing organic material in aqueous aerosols from glyoxal
143 following Woo et al.²⁷ GAMMA uses a detailed kinetic treatment of glyoxal chemistry and does not
144 assume chemical equilibrium.²⁵ Gas phase concentration of glyoxal was set to 4.68×10^9 molecule cm^{-3}
145 as previously used by Tsui et al.²⁶ The reaction of aqueous glyoxal with NH_4^+ to form light-absorbing
146 organic species was simulated using the kinetics of Schwieter et al.²⁸ for the base case and compared

147 with simulations where that overall rate constant was reduced to account for the effects of particle
148 pressure following the data in Figure 3. Simulations were performed for ammonium (bi)sulfate
149 particles at 65% RH and pH 2 with a diameter of 20, 40, 80, 160, or 320 nm, with a constant liquid
150 water content ($7.25 \times 10^{12} \text{ cm}^3 \text{ cm}^{-3}$) and surface area density ($10^{-4} \text{ cm}^2 \text{ cm}^{-3}$). No partitioning correction
151 was applied to take into consideration the possible Kelvin effect. In other words, to evaluate the effect
152 of the pressure, identical aqueous phase concentration of glyoxal was considered for the different size
153 bins. A 12-hour time period (dawn to dusk) was simulated. Ambient temperature was set to vary
154 sinusoidally through the day with a half-period of 12 h, with the minimum temperature 298.15K at
155 dawn and dusk and maximum temperature 303.15K at midday. Photochemical rate constants were set
156 following McNeill et al.²⁵

157 **Results and Discussion**

158 **Influence of pressure on the formation of glyoxal reaction products.** Assuming a liquid particle
159 and the known surface tension (γ) (e.g., 72.74 mN m⁻¹ for water, 44.4 mN m⁻¹ for SOA at 20°C),²⁹ the
160 effective pressure inside nanometre-sized particles can be calculated using the Young-Laplace
161 equation ($\Delta P = 2\gamma / r$, with r representing the radius of the particle) (Figure 1A). It should be pointed
162 out the surface tension of nanoparticles remains basically unknown and only the surface tension of
163 large aerosols can be determined. Hence, surface tension of alpha-pinene-derived SOA and pure water
164 were selected as lower and upper limits, respectively, to probe the impact of the pressure. Indeed,
165 earlier studies have shown that atmospherically relevant particles, including inorganic and organic
166 species, have surface tension within this range.²⁹⁻³³ Besides surface tension, other parameters can
167 influence the pressure, such as the phase state and/or chemical composition of the particles. For
168 example, the surface tension of dissolved SOA from the oxidation of biogenic compounds can be
169 reduced by a factor of two compared to pure water.²⁹ According to various studies, biogenic SOA
170 particles produced in laboratory chambers or observed in the ambient atmosphere may exist in various
171 solid and liquid forms.³⁴⁻³⁶ However, nanometre-sized organic aerosols remain liquid under most
172 environmental conditions.³⁶⁻³⁸ To investigate the impact of pressure on atmospheric chemical reactions
173 that occur within the particles, we studied the reaction between glyoxal and ammonium sulphate under

174 different pressures ranging from 1 atm to 500 atm: 0.1, 12.5, 25 and 50 MPa, corresponding to coarse
175 particles and to fine aerosol particles of 23, 12 and 6 nm in diameter, respectively (diameters
176 calculated assuming a liquid droplet with a surface tension of pure water). As previously reported,
177 products formed from the glyoxal-ammonium sulphate reaction absorb light in the UV and visible
178 wavelengths providing a convenient way to follow the reaction (Figures 1 and S1-S4).^{19,20,39} Figure 1B
179 shows the time evolution of the UV absorption spectra of a solution initially containing 0.25, 0.5, 1
180 and 2 M glyoxal mixed with 2 M of ammonium sulphate ((NH₄)₂SO₄) up to 24 hours, corresponding
181 to experimental conditions conducted under atmospheric pressure (i.e., 1 atm internal pressure).²⁰ The
182 resulting solution is weakly acidic (pH ~ 4), thus simulating aqueous tropospheric aerosol particles.
183 The absorbance of solutions at atmospheric pressure increased with time. Under high pressures, a
184 significant decrease in the total absorbance is observed for all conditions investigated in this study
185 (Figures 1C & 1D; S2). Already after 3h, the difference between experiments conducted at
186 atmospheric pressure and 50 MPa experiments is significant (i.e., Abs_{SP50}/Abs_{SP0.1} = 0.66 ± 0.02)
187 underlying the impact of increased pressure on the rate of glyoxal's reaction under slightly acidic
188 aqueous conditions. Interestingly, related reactions between carbonyls and amines have been studied
189 in the context of food science and a retarding effect of high (400 MPa) pressure was demonstrated.⁴⁰⁻
190 ⁴² This observation is consistent with our results, although we find an effect on the reaction of glyoxal
191 with ammonium sulphate at much milder pressures e.g., a slowing down by a factor of 2 at 25 MPa.
192 This proves that pressure can already have a pronounced effect in a relevant size range for atmospheric
193 aerosols. It is important to point out that in this study we have explored the effect of the pressure in
194 bulk solution in a closed system, i.e., no partitioning was considered. As a result, the decreasing rate
195 constant is only due to the effect of the pressure on the chemical processes. Additional studies are
196 required to relate what we observed in bulk solution to aerosol particles.

197 Ultra-performance liquid chromatography coupled with hybrid quadrupole Orbitrap mass
198 spectrometry analysis, performed in negative and positive modes, shows the presence of a wide
199 variety of reaction products (Figure 2A). The major reaction products, detected by their protonated
200 ions and consistent with other studies that form through the iminum pathway,^{19,20,22,24,43} (i.e., imidazole
201 (C₃H₅N₂⁺), imidazole-2-carboxaldehyde (C₄H₅ON₂⁺), hydrated imidazole-2-carboxaldehyde

202 ($\text{C}_4\text{H}_7\text{O}_2\text{N}_2^+$), are observed in all the experiments. This product distribution is consistent with the
203 existing literature, where high-molecular-weight organic compounds, formed by accretion reactions,
204 have been observed.^{12,19,20,43} Although the reaction products are similar in our study, samples exposed
205 to high pressures exhibit much lower product yields compared to the atmospheric pressure samples
206 (Figure 2A). More specifically, concentrations of the primary products, such as imidazole, reduced by
207 a factor of 2 after 24 hours, further highlighting the impact of pressure on this chemical system (Figure
208 2B). As in the Maillard reaction,^{41,44} chemical processes leading to the formation of such products
209 increase the volume of reaction (i.e., $\Delta V > 0$). Therefore, at higher pressure, the product formation is
210 reduced. In addition, formation of N-containing oligomers is also significantly suppressed by the
211 pressure (~ 40% after 24h). For example, the formation of $\text{C}_6\text{H}_{10}\text{O}_6\text{N}^+$ dimer is strongly reduced under
212 high pressures (Figure 2). Finally, it is noted that the glyoxal products formed from aldol/acetal
213 oligomerization were not observed in either the atmospheric pressure or the high-pressure samples.
214 Overall, the results obtained in this study reveal that the Laplace pressure, i.e., the pressure within
215 atmospheric particles, can strongly influence the multiphase processes involved in the formation and
216 growth of SOA.

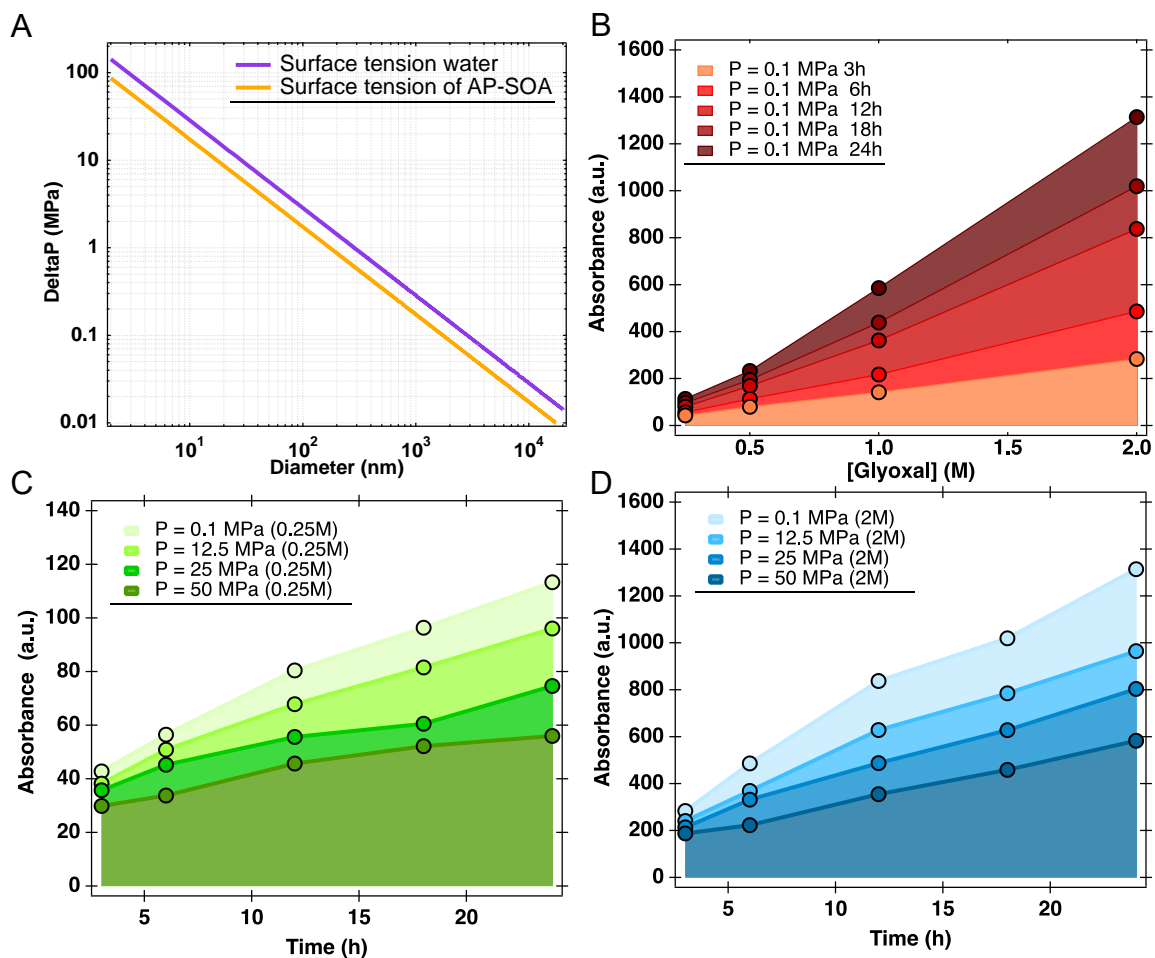
217 **Particle size-dependence kinetics.** As the light-absorbing compounds absorb light at 290 nm (Figure
218 S3), monitoring the evolution of this absorbance band provides insight into the overall kinetics of the
219 reaction between glyoxal and ammonium cations. The reactions are first order (Figure S4) within the
220 first 24 hours, which is consistent with an earlier study.²⁰ Therefore, for each set of experiments (i.e.,
221 four concentrations at a given pressure and four concentrations at atmospheric pressure), where each
222 condition was repeated at least three times, a global rate constant (k_{obs}) can be obtained. As shown in
223 Figure 3A, a pressure-dependent rate constant is determined, using the average k_{obs} determined for
224 each pressure. Using linear regression, particle size-dependence of the rate constant can be obtained,
225 as shown in Figure 3B. Two surface tension values were selected to obtain the rate constant as a
226 function of particle size: the surface tension of water (72.74 mN m^{-1}), which represents an upper limit,
227 and the surface tension of α -pinene SOA, which is formed under humid conditions (44.4 mN m^{-1}).²⁹
228 α -pinene-derived SOA is used as model SOA because monoterpenes are among the most important

229 SOA precursors on a global scale.^{45,46} Therefore, for ultrafine particles, i.e., < 100 nm, the reduction
230 of glyoxal chemistry is important, indicating that chemical processes identical or similar to those
231 involved in the heterogeneous chemistry of the dicarbonyls, can be strongly reduced in ultrafine
232 atmospheric aerosols.

233 To further illustrate particle size-dependence chemistry, the photochemical box model
234 GAMMA was used to simulate imidazole formation as a function of particle size (and hence pressure),
235 The calculations were performed in discrete size bins (i.e., 20, 40, 80, 160, and 320 nm), for 12 hours
236 (Figure 4).^{25,27,47} The simulations show that the pressure effect on the formation of imidazole and other
237 brown carbon species is negligible, for the largest size bin (i.e., 320 nm). However, the heterogeneous
238 process is greatly reduced when the pressure within the nanometre-sized particles increases. For
239 example, the formation of glyoxal reaction products is reduced by 20% for the smallest size bin (i.e.,
240 20 nm). This further underlines that chemical processes that are expected to grow ultrafine particles⁴⁸
241 are likely to be strongly influenced by their high internal pressure.

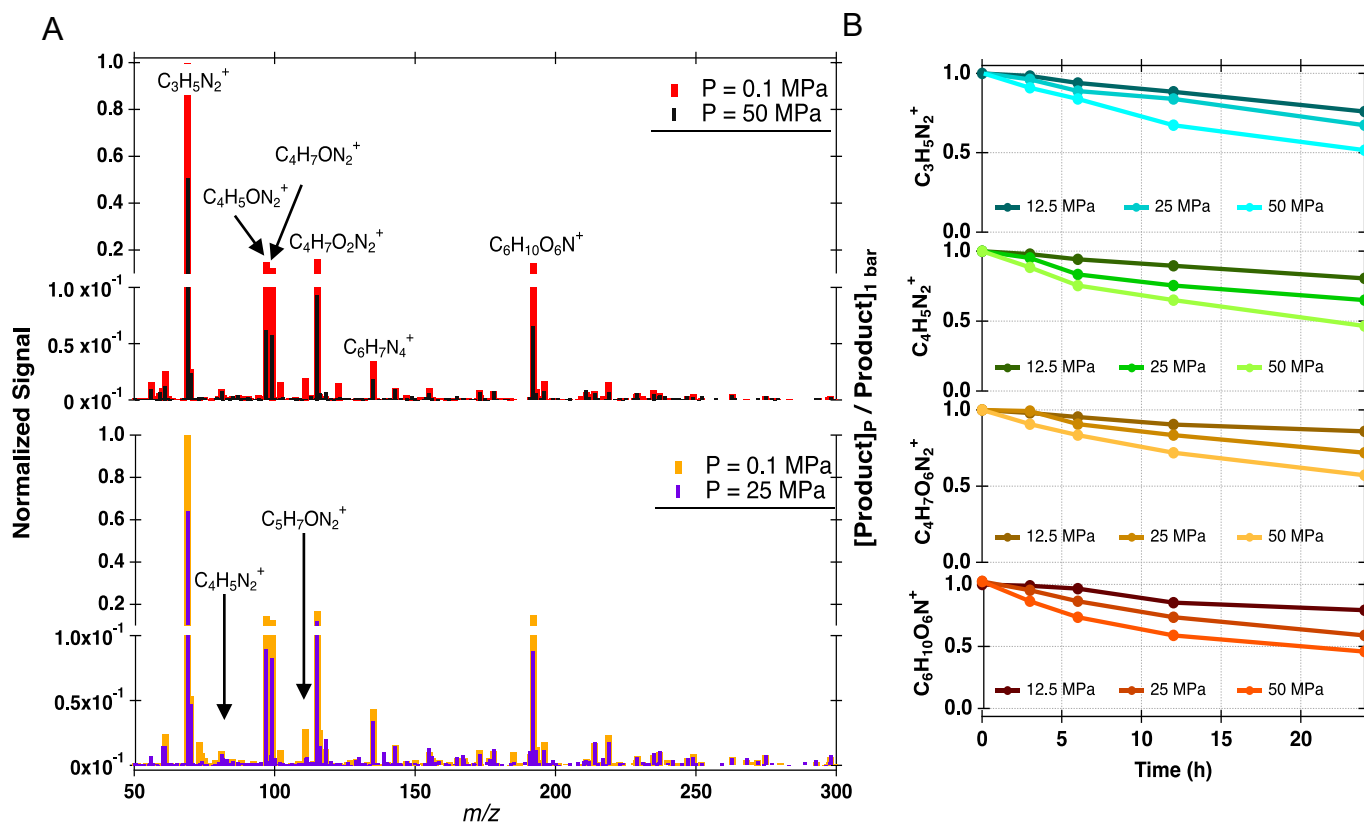
242 By studying an important chemical reaction under relevant atmospheric conditions, we showed that
243 the high pressure inside nanometre-sized aerosol particles is a key property that has not been
244 considered hitherto and that can have a significant influence on the chemical processes governing
245 atmospheric particle growth and evolution. More importantly we demonstrated that pressures can have
246 a noticeable effect at much milder pressures (~ 1-2 order of magnitude lower) than has been studied
247 before. Such pressures are highly relevant for atmospheric aerosols. However, it is important to note
248 that due to the relative short lifetime of nanoparticles (i.e., from a few hours to a day), the pressure
249 would have a noticeable effect for chemical reactions that are greatly impacted by the Laplace
250 pressure with rate constant comparable or shorter than the aerosol lifetime. Considering the Evans-
251 Polanyi principle, Le Noble and co-workers⁴⁹ have derived a function to represent the reaction profile
252 for a one-step reaction. By using such an approach, it is possible to evaluate the impact of the pressure
253 on changes in the transition state. As we studied a global reaction, it was not possible to isolate a
254 single reaction step using the analytical techniques employed by Le Noble et al.⁴⁹ However, based on
255 the existing literature we can derive some information providing hints that identify which reaction step
256 may have been mostly impacted by the pressure.^{8,50} For example, the breaking of bonds within a

257 reaction mechanism involves the separation of atoms from each other from covalent distances to van
258 der Waals distances. In fact, the transformation of NH_4^+ to H^+ and NH_3 , which was identified to be a
259 key state of the investigated chemistry,^{19,24} is known to be hindered by pressure (i.e., $\Delta V = 7 \text{ cm}^3 \text{ mol}^{-1}$)^{50,51}, and might explain the observation made here. While we found a negative effect here for this
260 specific reaction on the formation and growth of SOA, other potentially important particle phase
261 reactions, especially those with negative reaction volumes and/or negative activation volumes, could
262 be strongly promoted by pressure.^{1,22} The extensive literature on the effects of pressure on organic and
263 inorganic chemical reactions in solutions strongly suggests that several types of atmospheric reactions
264 could also be influenced by pressure.⁸ For example, nucleophilic substitution reactions of various
265 types of organic compounds at high pressure are favoured because ionisation reactions in the transition
266 state of the reaction cause negative activation volumes. While the experiments performed in this work
267 show a clear impact of the pressure, additional experiments using aerosol droplets are required to further
268 confirm the results presented here. Indeed, interfacial chemistry, gas-liquid exchanges i.e., processes not
269 considered here, may also be affected by the pressure in addition to the “bulk” chemical reaction kinetics
270 and equilibria. Overall, our results provide information about the potentially critical influence of
271 pressure on the chemistry occurring within atmospheric nanoparticles. While such processes have not
272 been reported before, this work emphasizes the need to consider particle phase processing under
273 atmospherically relevant conditions.
274
275

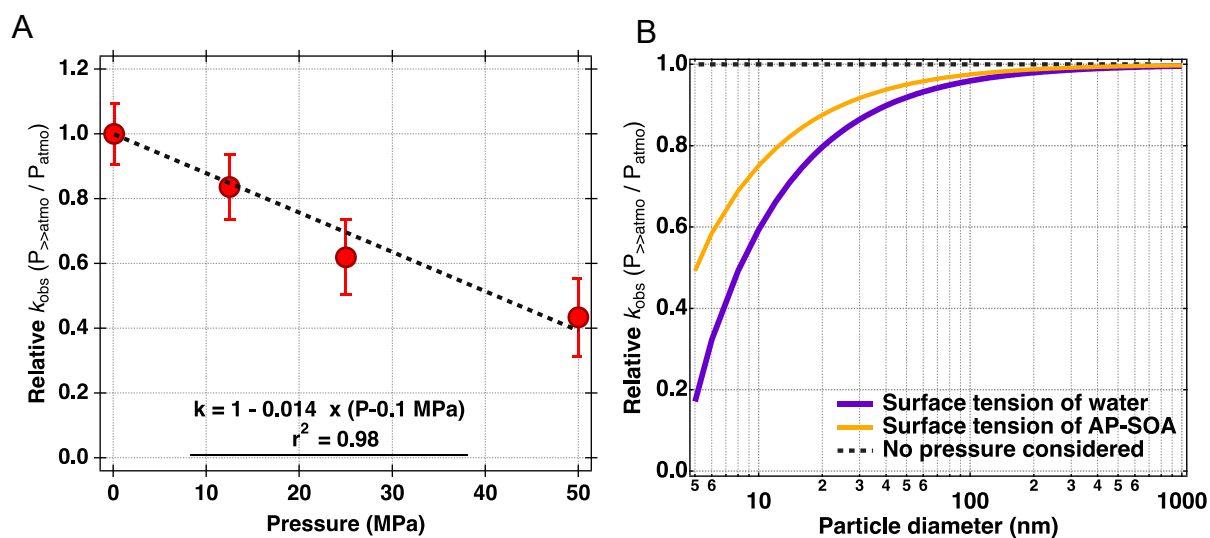


277

278 **Figure 1.** (A) Pressure inside 2 to 1000 nm aerosol particles with surface tension of water and α -pinene
 279 SOA. (B) Evolution of the absorbance (non-cumulative) of light-absorbing glyoxal reaction products at
 280 different reaction time and as function of glyoxal concentration. Non-cumulative absorbance of light-
 281 absorbing glyoxal reaction products at different pressures of (C) 0.25 M glyoxal/ 2 M AS and (D) 2 M
 282 glyoxal/ 2 M AS as a function of reaction time.



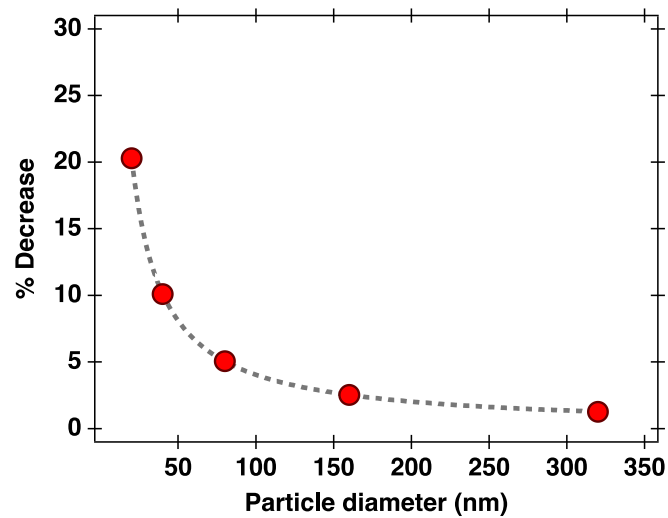
283 **Figure 2.** (A) Impact of the pressure on the chemical composition of organic products from the reaction
 284 of glyoxal with ammonium sulphate measured by UPLC-(+)ESI-Orbitrap. Mass spectra were averaged
 285 across the chromatogram and background subtracted (i.e., water samples served as blank). (B) Evolution
 286 of the relative concentration ($[Product]_{P \gg 1 \text{ atm}} / [Product]_{P=1 \text{ atm}}$) of the main reaction products as a
 287 function of time.
 288



289

290 **Figure 3.** (A) Relative glyoxal/AS reaction rate constant of light-absorbing product formation as a
 291 function of pressure. The overall uncertainty of the relative rate constant is 0.074 (one standard
 292 deviation). (B) Relative glyoxal/AS reaction rate constant as a function of aerosol particle diameter
 293 considering different aerosol surface tension.

294



295

296 **Figure 4.** Decrease of the formation of glyoxal reaction products as a function of particle size
297 diameter. Simulations were performed using GAMMA for different size bins diameters (e.g., 20, 40,
298 80, 160, and 320 nm) and under Eastern US rural conditions.

299 ASSOCIATED CONTENT

300 Figure S1 shows the absorbance of light-absorbing glyoxal oxidation products at different reaction
301 time and pressure. Figure S2 displays the relative absorbance of light-absorbing glyoxal oxidation
302 products under the different experimental conditions used in this study. Figure S3 shows the
303 absorption spectra of glyoxal products after 24 hours. Figure S4 shows the first-order kinetic fit for the
304 different experiments performed in this study. This material is available free of charge via the Internet
305 at <http://pubs.acs.org/>.

306

307 AUTHOR INFORMATION

308 **Corresponding Author**

309 *E-mail (M. R.): matthieu.riva@ircelyon.univ-lyon1.fr

310 *E-mail (T. H.): t.hoffmann@uni-mainz.de

311 *E-mail (C. G.): christian.george@ircelyon.univ-lyon1.fr

312 **Funding Sources**

313 This work is funded in part by the European Research Council (ERC-StG MAARvEL, grant nr 852161),
314 and by the Deutsche Forschungsgemeinschaft (DFG, HO 1748/19-1)

315

316 ACKNOWLEDGMENT

317 The authors wish to thank the European Research Council (ERC-StG), the Deutsche
318 Forschungsgemeinschaft and the University of Lyon for financial support. S.A.N. thanks the Université
319 Claude Bernard Lyon 1 for providing him with a visiting professorship in the summer of 2018.

320 ASSOCIATED CONTENT

321 Figure S1 shows the experimental device (high-pressure vessel) used in this study. This material
322 is available free of charge via the Internet at <http://pubs.acs.org/>.

323

- 325 (1) Hallquist, M.; Wenger, J. C.; Baltensperger, U.; Rudich, Y.; Simpson, D.; Claeys, M.;
 326 Dommen, J.; Donahue, N. M.; George, C.; Goldstein, A. H.; Hamilton, J. F.; Herrmann, H.;
 327 Hoffmann, T.; Iinuma, Y.; Jang, M.; Jenkin, M. E.; Jimenez, J. L.; Kiendler-Scharr, A.; Maenhaut, W.;
 328 McFiggans, G.; Mentel, Th. F.; Monod, A.; Prévôt, A. S. H.; Seinfeld, J. H.; Surratt, J. D.;
 329 Szmigielski, R.; Wildt, J. The Formation, Properties and Impact of Secondary Organic Aerosol:
 330 Current and Emerging Issues. *Atmospheric Chemistry and Physics* **2009**, 9 (14), 5155–5236.
 331 <https://doi.org/10.5194/acp-9-5155-2009>.
- 332 (2) Albrecht, B. A. Aerosols, Cloud Microphysics, and Fractional Cloudiness. *Science* **1989**, 245
 333 (4923), 1227–1230. <https://doi.org/10.1126/science.245.4923.1227>.
- 334 (3) Twomey, S. The Influence of Pollution on the Shortwave Albedo of Clouds. *Journal of the*
 335 *Atmospheric Sciences* **1977**, 34 (7), 1149–1152. [https://doi.org/10.1175/1520-0469\(1977\)034<1149:TIOPOT>2.0.CO;2](https://doi.org/10.1175/1520-0469(1977)034<1149:TIOPOT>2.0.CO;2).
- 337 (4) Gakidou, E.; Afshin, A.; Abajobir, A. A.; Abate, K. H.; Abbafati, C.; Abbas, K. M.; Abd-
 338 Allah, F.; Abdulle, A. M.; Abera, S. F.; Aboyans, V.; Abu-Raddad, L. J.; Abu-Rmeileh, N. M. E.;
 339 Abyu, G. Y.; Adedeji, I. A.; Adetokunboh, O.; Afarideh, M.; Agrawal, A.; Agrawal, S.; Ahmadiéh,
 340 H.; Ahmed, M. B.; Aichour, M. T. E.; Aichour, A. N.; Aichour, I.; Akinyemi, R. O.; Akseer, N.;
 341 Alahdab, F.; Al-Aly, Z.; Alam, K.; Alam, N.; Alam, T.; Alasfoor, D.; Alene, K. A.; Ali, K.; Alizadeh-
 342 Navaei, R.; Alkerwi, A.; Alla, F.; Allebeck, P.; Al-Raddadi, R.; Alsharif, U.; Altirkawi, K. A.; Alvis-
 343 Guzman, N.; Amare, A. T.; Amini, E.; Ammar, W.; Amoako, Y. A.; Ansari, H.; Antó, J. M.; Antonio,
 344 C. A. T.; Anwari, P.; Arian, N.; Ärnlöv, J.; Artaman, A.; Aryal, K. K.; Asayesh, H.; Asgedom, S. W.;
 345 Atey, T. M.; Avila-Burgos, L.; Avokpaho, E. F. G. A.; Awasthi, A.; Azzopardi, P.; Bacha, U.;
 346 Badawi, A.; Balakrishnan, K.; Ballew, S. H.; Barac, A.; Barber, R. M.; Barker-Collo, S. L.;
 347 Bärnighausen, T.; Barquera, S.; Barregard, L.; Barrero, L. H.; Batis, C.; Battle, K. E.; Baumgarner, B.
 348 R.; Baune, B. T.; Beardsley, J.; Bedi, N.; Beghi, E.; Bell, M. L.; Bennett, D. A.; Bennett, J. R.;
 349 Bensenor, I. M.; Berhane, A.; Berhe, D. F.; Bernabé, E.; Betsu, B. D.; Beuran, M.; Beyene, A. S.;
 350 Bhansali, A.; Bhutta, Z. A.; Bicer, B. K.; Bikbov, B.; Birungi, C.; Biryukov, S.; Blosser, C. D.;
 351 Boneya, D. J.; Bou-Orm, I. R.; Brauer, M.; Breitborde, N. J. K.; Brenner, H.; Brugha, T. S.; Bulto, L.
 352 N. B.; Butt, Z. A.; Cahuana-Hurtado, L.; Cárdenas, R.; Carrero, J. J.; Castañeda-Orjuela, C. A.;
 353 Catalá-López, F.; Cercy, K.; Chang, H.-Y.; Charlson, F. J.; Chimed-Ochir, O.; Chisumpa, V. H.;
 354 Chittheer, A. A.; Christensen, H.; Christopher, D. J.; Cirillo, M.; Cohen, A. J.; Comfort, H.; Cooper,
 355 C.; Coresh, J.; Cornaby, L.; Cortesi, P. A.; Criqui, M. H.; Crump, J. A.; Dandona, L.; Dandona, R.;
 356 das Neves, J.; Davey, G.; Davitoiu, D. V.; Davletov, K.; de Courten, B.; Defo, B. K.; Degenhardt, L.;
 357 Deiparine, S.; Dellavalle, R. P.; Deribe, K.; Deshpande, A.; Dharmaratne, S. D.; Ding, E. L.;
 358 Djalalinia, S.; Do, H. P.; Dokova, K.; Doku, D. T.; Donkelaar, A. van; Dorsey, E. R.; Driscoll, T. R.;
 359 Dubey, M.; Duncan, B. B.; Duncan, S.; Ebrahimi, H.; El-Khatib, Z. Z.; Enayati, A.; Endries, A. Y.;
 360 Ermakov, S. P.; Erskine, H. E.; Eshrati, B.; Eskandarieh, S.; Esteghamati, A.; Estep, K.; Faraon, E. J.
 361 A.; Farinha, C. S. e S.; Faro, A.; Farzadfar, F.; Fay, K.; Feigin, V. L.; Fereshtehnejad, S.-M.;
 362 Fernandes, J. C.; Ferrari, A. J.; Feyissa, T. R.; Filip, I.; Fischer, F.; Fitzmaurice, C.; Flaxman, A. D.;
 363 Foigt, N.; Foreman, K. J.; Frostad, J. J.; Fullman, N.; Fürst, T.; Furtado, J. M.; Ganji, M.; Garcia-
 364 Basteiro, A. L.; Gebrehiwot, T. T.; Geleijnse, J. M.; Geleto, A.; Gemechu, B. L.; Gesesew, H. A.;
 365 Gething, P. W.; Ghajar, A.; Gibney, K. B.; Gill, P. S.; Gillum, R. F.; Giref, A. Z.; Gishu, M. D.;
 366 Giussani, G.; Godwin, W. W.; Gona, P. N.; Goodridge, A.; Gopalani, S. V.; Goryakin, Y.; Goulart, A.
 367 C.; Graetz, N.; Gugnani, H. C.; Guo, J.; Gupta, R.; Gupta, T.; Gupta, V.; Gutiérrez, R. A.; Hachinski,
 368 V.; Hafezi-Nejad, N.; Hailu, G. B.; Hamadeh, R. R.; Hamidi, S.; Hammami, M.; Handal, A. J.;
 369 Hankey, G. J.; Hanson, S. W.; Harb, H. L.; Hareri, H. A.; Hassanvand, M. S.; Havmoeller, R.;
 370 Hawley, C.; Hay, S. I.; Hedayati, M. T.; Hendrie, D.; Heredia-Pi, I. B.; Hernandez, J. C. M.; Hoek, H.
 371 W.; Horita, N.; Hosgood, H. D.; Hostiuc, S.; Hoy, D. G.; Hsairi, M.; Hu, G.; Huang, J. J.; Huang, H.;
 372 Ibrahim, N. M.; Iburg, K. M.; Ikeda, C.; Inoue, M.; Irvine, C. M. S.; Jackson, M. D.; Jacobsen, K. H.;
 373 Jahanmehr, N.; Jakovljevic, M. B.; Jauregui, A.; Javanbakht, M.; Jeemon, P.; Johansson, L. R. K.;
 374 Johnson, C. O.; Jonas, J. B.; Jürisson, M.; Kabir, Z.; Kadel, R.; Kahsay, A.; Kamal, R.; Karch, A.;
 375 Karema, C. K.; Kasaeian, A.; Kassebaum, N. J.; Kastor, A.; Katikireddi, S. V.; Kawakami, N.;
 376 Keiyoro, P. N.; Kelbore, S. G.; Kemmer, L.; Kengne, A. P.; Kesavachandran, C. N.; Khader, Y. S.;
 377 Khalil, I. A.; Khan, E. A.; Khang, Y.-H.; Khosravi, A.; Khubchandani, J.; Kiadaliri, A. A.; Kieling,

378 C.; Kim, J. Y.; Kim, Y. J.; Kim, D.; Kimokoti, R. W.; Kinfu, Y.; Kisa, A.; Kissimova-Skarbek, K. A.;
 379 Kivimaki, M.; Knibbs, L. D.; Knudsen, A. K.; Kopec, J. A.; Kosen, S.; Koul, P. A.; Koyanagi, A.;
 380 Kravchenko, M.; Krohn, K. J.; Kromhout, H.; Kumar, G. A.; Kutz, M.; Kyu, H. H.; Lal, D. K.; Lalloo,
 381 R.; Lallukka, T.; Lan, Q.; Lansingh, V. C.; Larsson, A.; Lee, P. H.; Lee, A.; Leigh, J.; Leung, J.; Levi,
 382 M.; Levy, T. S.; Li, Y.; Li, Y.; Liang, X.; Liben, M. L.; Linn, S.; Liu, P.; Lodha, R.; Logroscino, G.;
 383 Looker, K. J.; Lopez, A. D.; Lorkowski, S.; Lotufo, P. A.; Lozano, R.; Lunevicius, R.; Macarayan, E.
 384 R. K.; Magdy Abd El Razek, H.; Magdy Abd El Razek, M.; Majdan, M.; Majdzadeh, R.; Majeed, A.;
 385 Malekzadeh, R.; Malhotra, R.; Malta, D. C.; Mamun, A. A.; Manguerra, H.; Mantovani, L. G.;
 386 Mapoma, C. C.; Martin, R. V.; Martinez-Raga, J.; Martins-Melo, F. R.; Mathur, M. R.; Matsushita, K.;
 387 Matzopoulos, R.; Mazidi, M.; McAlinden, C.; McGrath, J. J.; Mehata, S.; Mehndiratta, M. M.; Meier,
 388 T.; Melaku, Y. A.; Memiah, P.; Memish, Z. A.; Mendoza, W.; Mengesha, M. M.; Mensah, G. A.;
 389 Mensink, G. B. M.; Mereta, S. T.; Meretoja, T. J.; Meretoja, A.; Mezgebe, H. B.; Micha, R.; Milllear,
 390 A.; Miller, T. R.; Minnig, S.; Mirarefin, M.; Mirrahimov, E. M.; Misganaw, A.; Mishra, S. R.;
 391 Mohammad, K. A.; Mohammed, K. E.; Mohammed, S.; Mohan, M. B. V.; Mokdad, A. H.; Monasta,
 392 L.; Montico, M.; Moradi-Lakeh, M.; Moraga, P.; Morawska, L.; Morrison, S. D.; Mountjoy-Venning,
 393 C.; Mueller, U. O.; Mullany, E. C.; Muller, K.; Murthy, G. V. S.; Musa, K. I.; Naghavi, M.; Naheed,
 394 A.; Nangia, V.; Natarajan, G.; Negoi, R. I.; Negoi, I.; Nguyen, C. T.; Nguyen, Q. L.; Nguyen, T. H.;
 395 Nguyen, G.; Nguyen, M.; Nichols, E.; Ningrum, D. N. A.; Nomura, M.; Nong, V. M.; Norheim, O. F.;
 396 Norrving, B.; Noubiap, J. J. N.; Obermeyer, C. M.; Ogbo, F. A.; Oh, I.-H.; Oladimeji, O.; Olagunju,
 397 A. T.; Olagunju, T. O.; Olivares, P. R.; Olsen, H. E.; Olusanya, B. O.; Olusanya, J. O.; Opio, J. N.;
 398 Oren, E.; Ortiz, A.; Ota, E.; Owolabi, M. O.; Pa, M.; Pacella, R. E.; Pana, A.; Panda, B. K.; Panda-
 399 Jonas, S.; Pandian, J. D.; Papachristou, C.; Park, E.-K.; Parry, C. D.; Patten, S. B.; Patton, G. C.;
 400 Pereira, D. M.; Perico, N.; Pesudovs, K.; Petzold, M.; Phillips, M. R.; Pillay, J. D.; Piradov, M. A.;
 401 Pishgar, F.; Plass, D.; Pletcher, M. A.; Polinder, S.; Popova, S.; Poulton, R. G.; Pourmalek, F.; Prasad,
 402 N.; Purcell, C.; Qorbani, M.; Radfar, A.; Rafay, A.; Rahimi-Movaghar, A.; Rahimi-Movaghar, V.;
 403 Rahman, M. H. U.; Rahman, M. A.; Rahman, M.; Rai, R. K.; Rajsic, S.; Ram, U.; Rawaf, S.; Rehm, C.
 404 D.; Rehm, J.; Reiner, R. C.; Reitsma, M. B.; Remuzzi, G.; Renzaho, A. M. N.; Resnikoff, S.;
 405 Reynales-Shigematsu, L. M.; Rezaei, S.; Ribeiro, A. L.; Rivera, J. A.; Roba, K. T.; Rojas-Rueda, D.;
 406 Roman, Y.; Room, R.; Roshandel, G.; Roth, G. A.; Rothenbacher, D.; Rubagotti, E.; Rushton, L.;
 407 Sadat, N.; Safdarian, M.; Safi, S.; Safiri, S.; Sahathevan, R.; Salama, J.; Salomon, J. A.; Samy, A. M.;
 408 Sanabria, J. R.; Sanchez-Niño, M. D.; Sánchez-Pimienta, T. G.; Santomauro, D.; Santos, I. S.; Santric
 409 Milicevic, M. M.; Sartorius, B.; Satpathy, M.; Sawhney, M.; Saxena, S.; Schmidt, M. I.; Schneider, I.
 410 J. C.; Schutte, A. E.; Schwebel, D. C.; Schwendicke, F.; Seedat, S.; Sepanlou, S. G.; Serdar, B.;
 411 Servan-Mori, E. E.; Shaddick, G.; Shaheen, A.; Shahraz, S.; Shaikh, M. A.; Shamsipour, M.;
 412 Shamsizadeh, M.; Shariful Islam, S. M.; Sharma, J.; Sharma, R.; She, J.; Shen, J.; Shi, P.; Shibuya, K.;
 413 Shields, C.; Shiferaw, M. S.; Shigematsu, M.; Shin, M.-J.; Shiri, R.; Shirkoohi, R.; Shishani, K.;
 414 Shoman, H.; Shrimme, M. G.; Sigfusdottir, I. D.; Silva, D. A. S.; Silva, J. P.; Silveira, D. G. A.; Singh,
 415 J. A.; Singh, V.; Sinha, D. N.; Skiadaresi, E.; Slepak, E. L.; Smith, D. L.; Smith, M.; Sobaih, B. H. A.;
 416 Sobngwi, E.; Soneji, S.; Sorensen, R. J. D.; Sposato, L. A.; Sreeramareddy, C. T.; Srinivasan, V.;
 417 Steel, N.; Stein, D. J.; Steiner, C.; Steinke, S.; Stokes, M. A.; Strub, B.; Subart, M.; Sufiyan, M. B.;
 418 Suliankatchi, R. A.; Sur, P. J.; Swaminathan, S.; Sykes, B. L.; Szoeki, C. E. I.; Tabarés-Seisdedos, R.;
 419 Tadakamadla, S. K.; Takahashi, K.; Takala, J. S.; Tandon, N.; Tanner, M.; Tarekegn, Y. L.;
 420 Tavakkoli, M.; Tegegne, T. K.; Tehrani-Banihashemi, A.; Terkawi, A. S.; Tessema, B.; Thakur, J.;
 421 Thamsuwan, O.; Thankappan, K. R.; Theis, A. M.; Thomas, M. L.; Thomson, A. J.; Thrift, A. G.;
 422 Tillmann, T.; Tobe-Gai, R.; Tobollik, M.; Tollanes, M. C.; Tonelli, M.; Topor-Madry, R.; Torre, A.;
 423 Tortajada, M.; Touvier, M.; Tran, B. X.; Truelsen, T.; Tuem, K. B.; Tuzcu, E. M.; Tyrovolas, S.;
 424 Ukwaja, K. N.; Uneke, C. J.; Updike, R.; Uthman, O. A.; van Boven, J. F. M.; Varughese, S.;
 425 Vasankari, T.; Veerman, L. J.; Venkateswaran, V.; Venketasubramanian, N.; Violante, F. S.;
 426 Vladimirov, S. K.; Vlassov, V. V.; Vollset, S. E.; Vos, T.; Wadilo, F.; Wakayo, T.; Wallin, M. T.;
 427 Wang, Y.-P.; Weichenthal, S.; Weiderpass, E.; Weintraub, R. G.; Weiss, D. J.; Werdecker, A.;
 428 Westerman, R.; Whiteford, H. A.; Wiysonge, C. S.; Woldeyes, B. G.; Wolfe, C. D. A.; Woodbrook,
 429 R.; Workicho, A.; Xavier, D.; Xu, G.; Yadgir, S.; Yakob, B.; Yan, L. L.; Yaseri, M.; Yimam, H. H.;
 430 Yip, P.; Yonemoto, N.; Yoon, S.-J.; Yotebieng, M.; Younis, M. Z.; Zaidi, Z.; Zaki, M. E. S.; Zavala-
 431 Arciniega, L.; Zhang, X.; Zimsen, S. R. M.; Zipkin, B.; Zodpey, S.; Lim, S. S.; Murray, C. J. L.
 432 Global, Regional, and National Comparative Risk Assessment of 84 Behavioural, Environmental and

433 Occupational, and Metabolic Risks or Clusters of Risks, 1990–2016: A Systematic Analysis for the
434 Global Burden of Disease Study 2016. *The Lancet* **2017**, *390* (10100), 1345–1422.
435 [https://doi.org/10.1016/S0140-6736\(17\)32366-8](https://doi.org/10.1016/S0140-6736(17)32366-8).

436 (5) Shrivastava, M.; Cappa, C. D.; Fan, J.; Goldstein, A. H.; Guenther, A. B.; Jimenez, J. L.;
437 Kuang, C.; Laskin, A.; Martin, S. T.; Ng, N. L.; Petaja, T.; Pierce, J. R.; Rasch, P. J.; Roldin, P.;
438 Seinfeld, J. H.; Shilling, J.; Smith, J. N.; Thornton, J. A.; Volkamer, R.; Wang, J.; Worsnop, D. R.;
439 Zaveri, R. A.; Zelenyuk, A.; Zhang, Q. Recent Advances in Understanding Secondary Organic
440 Aerosol: Implications for Global Climate Forcing: Advances in Secondary Organic Aerosol. *Reviews*
441 *of Geophysics* **2017**, *55* (2), 509–559. <https://doi.org/10.1002/2016RG000540>.

442 (6) Jimenez, J. L.; Canagaratna, M. R.; Donahue, N. M.; Prevot, A. S. H.; Zhang, Q.; Kroll, J. H.;
443 DeCarlo, P. F.; Allan, J. D.; Coe, H.; Ng, N. L.; Aiken, A. C.; Docherty, K. S.; Ulbrich, I. M.;
444 Grieshop, A. P.; Robinson, A. L.; Duplissy, J.; Smith, J. D.; Wilson, K. R.; Lanz, V. A.; Hueglin, C.;
445 Sun, Y. L.; Tian, J.; Laaksonen, A.; Raatikainen, T.; Rautiainen, J.; Vaattovaara, P.; Ehn, M.;
446 Kulmala, M.; Tomlinson, J. M.; Collins, D. R.; Cubison, M. J.; E.; Dunlea, J.; Huffman, J. A.; Onasch,
447 T. B.; Alfarra, M. R.; Williams, P. I.; Bower, K.; Kondo, Y.; Schneider, J.; Drewnick, F.; Borrmann,
448 S.; Weimer, S.; Demerjian, K.; Salcedo, D.; Cottrell, L.; Griffin, R.; Takami, A.; Miyoshi, T.;
449 Hatakeyama, S.; Shimono, A.; Sun, J. Y.; Zhang, Y. M.; Dzepina, K.; Kimmel, J. R.; Sueper, D.;
450 Jayne, J. T.; Herndon, S. C.; Trimborn, A. M.; Williams, L. R.; Wood, E. C.; Middlebrook, A. M.;
451 Kolb, C. E.; Baltensperger, U.; Worsnop, D. R. Evolution of Organic Aerosols in the Atmosphere.
452 *Science* **2009**, *326* (5959), 1525–1529. <https://doi.org/10.1126/science.1180353>.

453 (7) Ibach, H. *Physics of Surfaces and Interfaces*; Springer: Berlin; New York, 2006.

454 (8) Drljaca, A.; Hubbard, C. D.; van Eldik, R.; Asano, T.; Basilevsky, M. V.; le Noble, W. J.
455 Activation and Reaction Volumes in Solution. 3. *Chemical Reviews* **1998**, *98* (6), 2167–2290.
456 <https://doi.org/10.1021/cr970461b>.

457 (9) Laidler, K. J.; King, M. C. Development of Transition-State Theory. *J. Phys. Chem.* **1983**, *87*
458 (15), 2657–2664. <https://doi.org/10.1021/j100238a002>.

459 (10) Chen, B.; Hoffmann, R.; Cammi, R. The Effect of Pressure on Organic Reactions in Fluids—a
460 New Theoretical Perspective. *Angew. Chem. Int. Ed.* **2017**, *56* (37), 11126–11142.
461 <https://doi.org/10.1002/anie.201705427>.

462 (11) Fu, T.-M.; Jacob, D. J.; Wittrock, F.; Burrows, J. P.; Vrekoussis, M.; Henze, D. K. Global
463 Budgets of Atmospheric Glyoxal and Methylglyoxal, and Implications for Formation of Secondary
464 Organic Aerosols. *Journal of Geophysical Research* **2008**, *113* (D15).
465 <https://doi.org/10.1029/2007JD009505>.

466 (12) Galloway, M. M.; Chhabra, P. S.; Chan, A. W. H.; Surratt, J. D.; Flagan, R. C.; Seinfeld, J. H.;
467 Keutsch, F. N. Glyoxal Uptake on Ammonium Sulphate Seed Aerosol: Reaction Products and
468 Reversibility of Uptake under Dark and Irradiated Conditions. *Atmos. Chem. Phys.* **2009**, *9* (10),
469 3331–3345. <https://doi.org/10.5194/acp-9-3331-2009>.

470 (13) Liggio, J. Reactive Uptake of Glyoxal by Particulate Matter. *J. Geophys. Res.* **2005**, *110*
471 (D10), D10304. <https://doi.org/10.1029/2004JD005113>.

472 (14) Kroll, J. H.; Ng, N. L.; Murphy, S. M.; Varutbangkul, V.; Flagan, R. C.; Seinfeld, J. H.
473 Chamber Studies of Secondary Organic Aerosol Growth by Reactive Uptake of Simple Carbonyl
474 Compounds. *J. Geophys. Res.* **2005**, *110* (D23), D23207. <https://doi.org/10.1029/2005JD006004>.

475 (15) Corrigan, A. L.; Hanley, S. W.; De Haan, D. O. Uptake of Glyoxal by Organic and Inorganic
476 Aerosol. *Environ. Sci. Technol.* **2008**, *42* (12), 4428–4433. <https://doi.org/10.1021/es7032394>.

477 (16) Haan, D. O. D.; Corrigan, A. L.; Smith, K. W.; Stroik, D. R.; Turley, J. J.; Lee, F. E.; Tolbert,
478 M. A.; Jimenez, J. L.; Cordova, K. E.; Ferrell, G. R. Secondary Organic Aerosol-Forming Reactions
479 of Glyoxal with Amino Acids. *Environ. Sci. Technol.* **2009**, *43* (8), 2818–2824.
480 <https://doi.org/10.1021/es803534f>.

481 (17) Ervens, B.; Volkamer, R. Glyoxal Processing by Aerosol Multiphase Chemistry: Towards a
482 Kinetic Modeling Framework of Secondary Organic Aerosol Formation in Aqueous Particles. *Atmos.*
483 *Chem. Phys.* **2010**, *10* (17), 8219–8244. <https://doi.org/10.5194/acp-10-8219-2010>.

484 (18) Trainic, M.; Abo Riziq, A.; Lavi, A.; Flores, J. M.; Rudich, Y. The Optical, Physical and
485 Chemical Properties of the Products of Glyoxal Uptake on Ammonium Sulfate Seed Aerosols. *Atmos.*
486 *Chem. Phys.* **2011**, *11* (18), 9697–9707. <https://doi.org/10.5194/acp-11-9697-2011>.

487 (19) Yu, G.; Bayer, A. R.; Galloway, M. M.; Korshavn, K. J.; Fry, C. G.; Keutsch, F. N. Glyoxal in

488 Aqueous Ammonium Sulfate Solutions: Products, Kinetics and Hydration Effects. *Environmental*
489 *Science & Technology* **2011**, *45* (15), 6336–6342. <https://doi.org/10.1021/es200989n>.

490 (20) Nozière, B.; Dziejczak, P.; Córdova, A. Products and Kinetics of the Liquid-Phase Reaction of
491 Glyoxal Catalyzed by Ammonium Ions (NH_4^+). *The Journal of Physical Chemistry A* **2009**, *113* (1),
492 231–237. <https://doi.org/10.1021/jp8078293>.

493 (21) Rossignol, S.; Aregahegn, K. Z.; Tinel, L.; Fine, L.; Nozière, B.; George, C. Glyoxal Induced
494 Atmospheric Photosensitized Chemistry Leading to Organic Aerosol Growth. *Environmental Science*
495 *& Technology* **2014**, *48* (6), 3218–3227. <https://doi.org/10.1021/es405581g>.

496 (22) Herrmann, H.; Schaefer, T.; Tilgner, A.; Styler, S. A.; Weller, C.; Teich, M.; Otto, T.
497 Tropospheric Aqueous-Phase Chemistry: Kinetics, Mechanisms, and Its Coupling to a Changing Gas
498 Phase. *Chemical Reviews* **2015**, *115* (10), 4259–4334. <https://doi.org/10.1021/cr500447k>.

499 (23) Volkamer, R.; San Martini, F.; Molina, L. T.; Salcedo, D.; Jimenez, J. L.; Molina, M. J. A
500 Missing Sink for Gas-Phase Glyoxal in Mexico City: Formation of Secondary Organic Aerosol.
501 *Geophys. Res. Lett.* **2007**, *34* (19), L19807. <https://doi.org/10.1029/2007GL030752>.

502 (24) Kampf, C. J.; Jakob, R.; Hoffmann, T. Identification and Characterization of Aging Products
503 in the Glyoxal/Ammonium Sulfate System – Implications for Light-Absorbing Material in
504 Atmospheric Aerosols. *Atmos. Chem. Phys.* **2012**, *12* (14), 6323–6333. [https://doi.org/10.5194/acp-12-](https://doi.org/10.5194/acp-12-6323-2012)
505 6323-2012.

506 (25) McNeill, V. F.; Woo, J. L.; Kim, D. D.; Schwier, A. N.; Wannell, N. J.; Sumner, A. J.;
507 Barakat, J. M. Aqueous-Phase Secondary Organic Aerosol and Organosulfate Formation in
508 Atmospheric Aerosols: A Modeling Study. *Environmental Science & Technology* **2012**, *46* (15),
509 8075–8081. <https://doi.org/10.1021/es3002986>.

510 (26) Tsui, W. G.; Woo, J. L.; McNeill, V. F. Impact of Aerosol-Cloud Cycling on Aqueous
511 Secondary Organic Aerosol Formation. *Atmosphere* **2019**, *10* (11), 666.
512 <https://doi.org/10.3390/atmos10110666>.

513 (27) Woo, J. L.; Kim, D. D.; Schwier, A. N.; Li, R.; McNeill, V. F. Aqueous Aerosol SOA
514 Formation: Impact on Aerosol Physical Properties. *Faraday Discuss.* **2013**, *165*, 357.
515 <https://doi.org/10.1039/c3fd00032j>.

516 (28) Schwier, A. N.; Sareen, N.; Mitroo, D.; Shapiro, E. L.; McNeill, V. F. Glyoxal-Methylglyoxal
517 Cross-Reactions in Secondary Organic Aerosol Formation. *Environ. Sci. Technol.* **2010**, *44* (16),
518 6174–6182. <https://doi.org/10.1021/es101225q>.

519 (29) Hritz, A. D.; Raymond, T. M.; Dutcher, D. D. A Method for the Direct Measurement of
520 Surface Tension of Collected Atmospherically Relevant Aerosol Particles Using Atomic Force
521 Microscopy. *Atmospheric Chemistry and Physics* **2016**, *16* (15), 9761–9769.
522 <https://doi.org/10.5194/acp-16-9761-2016>.

523 (30) Bzdek, B. R.; Power, R. M.; Simpson, S. H.; Reid, J. P.; Royall, C. P. Precise, Contactless
524 Measurements of the Surface Tension of Picolitre Aerosol Droplets. *Chem. Sci.* **2016**, *7* (1), 274–285.
525 <https://doi.org/10.1039/C5SC03184B>.

526 (31) Gray Bé, A.; Upshur, M. A.; Liu, P.; Martin, S. T.; Geiger, F. M.; Thomson, R. J. Cloud
527 Activation Potentials for Atmospheric α -Pinene and β -Caryophyllene Ozonolysis Products. *ACS Cent.*
528 *Sci.* **2017**, *3* (7), 715–725. <https://doi.org/10.1021/acscentsci.7b00112>.

529 (32) Schwier, A. N.; Viglione, G. A.; Li, Z.; Faye McNeill, V. Modeling the Surface Tension of
530 Complex, Reactive Organic–Inorganic Mixtures. *Atmos. Chem. Phys.* **2013**, *13* (21), 10721–10732.
531 <https://doi.org/10.5194/acp-13-10721-2013>.

532 (33) Shapiro, E. L.; Szprengiel, J.; Sareen, N.; Jen, C. N.; Giordano, M. R.; McNeill, V. F. Light-
533 Absorbing Secondary Organic Material Formed by Glyoxal in Aqueous Aerosol Mimics. *Atmos.*
534 *Chem. Phys.* **2009**, *9* (7), 2289–2300. <https://doi.org/10.5194/acp-9-2289-2009>.

535 (34) Bateman, A. P.; Gong, Z.; Liu, P.; Sato, B.; Cirino, G.; Zhang, Y.; Artaxo, P.; Bertram, A. K.;
536 Manzi, A. O.; Rizzo, L. V.; Souza, R. A. F.; Zaveri, R. A.; Martin, S. T. Sub-Micrometre Particulate
537 Matter Is Primarily in Liquid Form over Amazon Rainforest. *Nature Geoscience* **2016**, *9* (1), 34–37.
538 <https://doi.org/10.1038/ngeo2599>.

539 (35) Cappa, C. D.; Wilson, K. R. Evolution of Organic Aerosol Mass Spectra upon Heating:
540 Implications for OA Phase and Partitioning Behavior. *Atmospheric Chemistry and Physics* **2011**, *11*
541 (5), 1895–1911. <https://doi.org/10.5194/acp-11-1895-2011>.

542 (36) Virtanen, A.; Joutsensaari, J.; Koop, T.; Kannosto, J.; Yli-Pirilä, P.; Leskinen, J.; Mäkelä, J.

543 M.; Holopainen, J. K.; Pöschl, U.; Kulmala, M.; Worsnop, D. R.; Laaksonen, A. An Amorphous Solid
544 State of Biogenic Secondary Organic Aerosol Particles. *Nature* **2010**, *467* (7317), 824–827.
545 <https://doi.org/10.1038/nature09455>.

546 (37) Cheng, Y.; Su, H.; Koop, T.; Mikhailov, E.; Pöschl, U. Size Dependence of Phase Transitions
547 in Aerosol Nanoparticles. *Nature Communications* **2015**, *6* (1). <https://doi.org/10.1038/ncomms6923>.

548 (38) Virtanen, A.; Kannosto, J.; Kuuluvainen, H.; Arffman, A.; Joutsensaari, J.; Saukko, E.; Hao,
549 L.; Yli-Pirilä, P.; Tiitta, P.; Holopainen, J. K.; Keskinen, J.; Worsnop, D. R.; Smith, J. N.; Laaksonen,
550 A. Bounce Behavior of Freshly Nucleated Biogenic Secondary Organic Aerosol Particles.
551 *Atmospheric Chemistry and Physics* **2011**, *11* (16), 8759–8766. [https://doi.org/10.5194/acp-11-8759-](https://doi.org/10.5194/acp-11-8759-2011)
552 [2011](https://doi.org/10.5194/acp-11-8759-2011).

553 (39) Powelson, M. H.; Espelien, B. M.; Hawkins, L. N.; Galloway, M. M.; De Haan, D. O. Brown
554 Carbon Formation by Aqueous-Phase Carbonyl Compound Reactions with Amines and Ammonium
555 Sulfate. *Environ. Sci. Technol.* **2014**, *48* (2), 985–993. <https://doi.org/10.1021/es4038325>.

556 (40) De Vleeschouwer, K.; Van der Plancken, I.; Van Loey, A.; Hendrickx, M. E. The Effect of
557 High Pressure–High Temperature Processing Conditions on Acrylamide Formation and Other
558 Maillard Reaction Compounds. *Journal of Agricultural and Food Chemistry* **2010**, *58* (22), 11740–
559 11748. <https://doi.org/10.1021/jf102697b>.

560 (41) Moreno, F. J.; Molina, E.; Olano, A.; López-Fandiño, R. High-Pressure Effects on Maillard
561 Reaction between Glucose and Lysine. *J. Agric. Food Chem.* **2003**, *51* (2), 394–400.
562 <https://doi.org/10.1021/jf025731s>.

563 (42) Schwarzenbolz, U.; Förster, A.; Henle, T. Influence of High Hydrostatic Pressure on the
564 Reaction between Glyoxal and Lysine Residues. *Eur Food Res Technol* **2017**, *243* (8), 1355–1361.
565 <https://doi.org/10.1007/s00217-017-2846-x>.

566 (43) Hamilton, J. F.; Baeza-Romero, M. T.; Finessi, E.; Rickard, A. R.; Healy, R. M.; Peppe, S.;
567 Adams, T. J.; Daniels, M. J. S.; Ball, S. M.; Goodall, I. C. A.; Monks, P. S.; Borrás, E.; Muñoz, A.
568 Online and Offline Mass Spectrometric Study of the Impact of Oxidation and Ageing on Glyoxal
569 Chemistry and Uptake onto Ammonium Sulfate Aerosols. *Faraday Discussions* **2013**, *165*, 447.
570 <https://doi.org/10.1039/c3fd00051f>.

571 (44) Hawkins, L. N.; Lemire, A. N.; Galloway, M. M.; Corrigan, A. L.; Turley, J. J.; Espelien, B.
572 M.; De Haan, D. O. Maillard Chemistry in Clouds and Aqueous Aerosol As a Source of Atmospheric
573 Humic-Like Substances. *Environ. Sci. Technol.* **2016**, *50* (14), 7443–7452.
574 <https://doi.org/10.1021/acs.est.6b00909>.

575 (45) Jokinen, T.; Berndt, T.; Makkonen, R.; Kerminen, V.-M.; Junninen, H.; Paasonen, P.;
576 Stratmann, F.; Herrmann, H.; Guenther, A. B.; Worsnop, D. R.; Kulmala, M.; Ehn, M.; Sipilä, M.
577 Production of Extremely Low Volatile Organic Compounds from Biogenic Emissions: Measured
578 Yields and Atmospheric Implications. *Proceedings of the National Academy of Sciences* **2015**, *112*
579 (23), 7123–7128. <https://doi.org/10.1073/pnas.1423977112>.

580 (46) Kelly, J. M.; Doherty, R. M.; O’Connor, F. M.; Mann, G. W. The Impact of
581 Biogenic, Anthropogenic, and Biomass Burning Volatile Organic Compound Emissions on Regional
582 and Seasonal Variations in Secondary Organic Aerosol. *Atmospheric Chemistry and Physics* **2018**, *18*
583 (10), 7393–7422. <https://doi.org/10.5194/acp-18-7393-2018>.

584 (47) Woo, J. L.; McNeill, V. F. SimpleGAMMA v1.0 – a Reduced Model of Secondary Organic
585 Aerosol Formation in the Aqueous Aerosol Phase (AaSOA). *Geosci. Model Dev.* **2015**, *8* (6), 1821–
586 1829. <https://doi.org/10.5194/gmd-8-1821-2015>.

587 (48) Apsokardu, M. J.; Johnston, M. V. Nanoparticle Growth by Particle-Phase Chemistry.
588 *Atmospheric Chemistry and Physics* **2018**, *18* (3), 1895–1907. [https://doi.org/10.5194/acp-18-1895-](https://doi.org/10.5194/acp-18-1895-2018)
589 [2018](https://doi.org/10.5194/acp-18-1895-2018).

590 (49) Le Noble, W. J.; Miller, A. R.; Hamann, S. D. A Simple, Empirical Function Describing the
591 Reaction Profile, and Some Applications. *J. Org. Chem.* **1977**, *42* (2), 338–342.
592 <https://doi.org/10.1021/jo00422a035>.

593 (50) Asano, T.; Le Noble, W. J. Activation and Reaction Volumes in Solution. *Chem. Rev.* **1978**,
594 *78* (4), 407–489. <https://doi.org/10.1021/cr60314a004>.

595 (51) Stokes, R. The Apparent Molar Volumes of Aqueous Ammonia, Ammonium Chloride,
596 Aniline and Anilinium Chloride at 25°C and the Volume Changes on Ionization. *Aust. J. Chem.* **1975**,
597 *28* (10), 2109. <https://doi.org/10.1071/CH9752109>.

